Quantum Physics

Prof. V. Balskrishnan

Department of Physics

Indian Institute of Technology, Madras

Lecture No # 30

We continue with our study of perturbation theory. Now, the question is: does the 0 point energy of all these oscillators contribute? Because, each oscillator contributes an energy 1/2 h cross omega and you are now integrating over all possible omegas. The answer is, formally its infinite. Of course, if you put all the oscillators in the ground state and you have an infinite number of oscillators you integrate over all omega the answer is infinite. This called the energy of the vacuum. A proper treatment of this infinity is done only in quantum field theory when one knows how to take care of the 0 of energy. A crude answer would be to say: this is a reference level of energy. The fact that when you got nothing, you can set the energy to be = 0 in the vacuum, even though formally this calculation would give an infinite contribution. That's a rather facile argument and is not very satisfactory. It is resolved appropriately only in quantum field theory which is outside the purview of this course. But this 0 point energy's divergence is important. It does play a role. There are effects, by the way, which measure this 0 point energy. The fact is that this energy has a physical role to play. Since this has been raised, let me give 2 instances as to where it's going to play a role and how it's taken care of.

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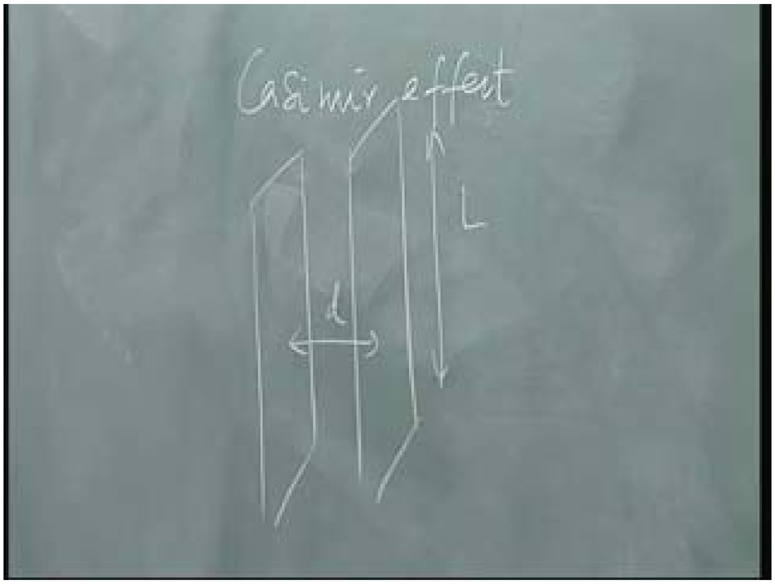

One of them has to do with the so called ‘Casimir effect’. It’s the following simple observation. Suppose, you have 2 parallel plates metallic plates in a vacuum and you place them parallel to each at a short distance, d from each other. The distance d is small compared to the linear dimension, L of the plates. You place them close to each other and have nothing inside. Just a vacuum. Because of the 0 point energy in the system, there actually exists an attractive force between these 2 plates due to the fluctuations of the electromagnetic field. So although you don’t have any actual applied field in this region, there are these fluctuations of the electric field in the ground state. We saw in the very simple example of electrodynamics that the electric field for instance, would vanish at the 2 end points or at the 2 plates. In between, it can still have a mean square value which is non-zero. Because it’s a potential energy, you take minus its gradient; you are going to get a force. There exist a force between these 2 plates and there is an attractive force. This is called the Casimir effect.

It can be computed exactly and in the late 50’s in the last century, it was actually measured. Since then, refined experiments have been done which corroborate the quantum electrodynamic calculation. So this effect comes directly from the 0 point energy. That’s a physical effect. The other effect which is very well-known in spectroscopy is that the energy levels of atoms are shifted slightly due to these quantum fluctuations. In the ground state you don’t see this thing at all. But it will appear in the excited states of the atom and it’s called the Lamb shift. This has again been measured. its known to a very large number of decimal places and has been corroborated. This again is the manifestation of the zero point energy of a system. There are other problems in quantum field theory and other formal divergences but the zero point energy is the first of these for these oscillators and, yes. it does play a role. Except when we compute the energy in black body radiation, you can see that the contribution from the denominator the partition function in the numerator of this 1/2 h cross omega got canceled out. So when you are actually computing the average energy, this contribution has got canceled out and we talk only about what’s left which is frequency dependent. so in that sense, this has been hidden. The zero-point energy has been hidden in that calculation. Now let me recall to you what we had got to in perturbation theory.

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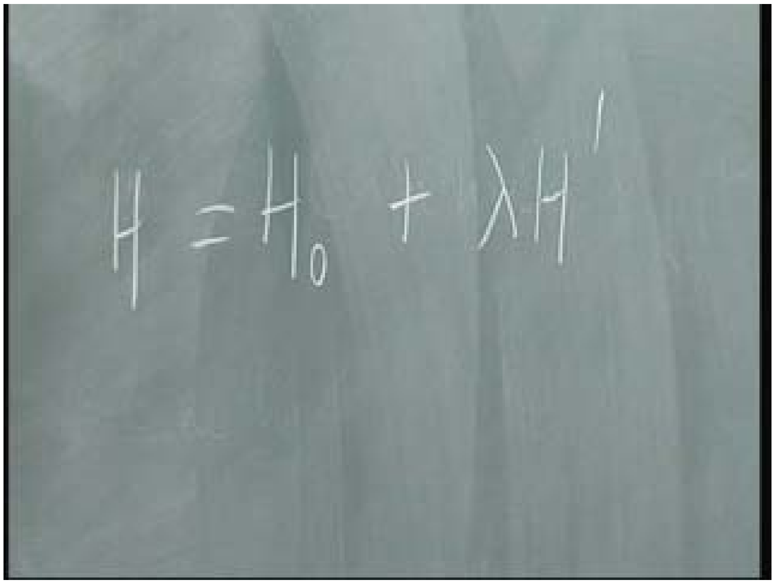

$$H = H_0 + \lambda H'$$

So we had non-degenerate set of energy levels for a Hamiltonian H_0 and I added to this a perturbation lambda H prime. That was my total Hamiltonian. The idea was, in principle we assume that we know how to solve for the eigenvalues and eigenfunctions of H_0. They form a complete set and then the question is: what are the exact energy eigenvalues and eigenfunctions? The answer in general, is that if H prime does not commute with the H_0, there is no simple way of writing down an explicit general formula for what the exact values of the eigenfunctions and eigenvalues are.

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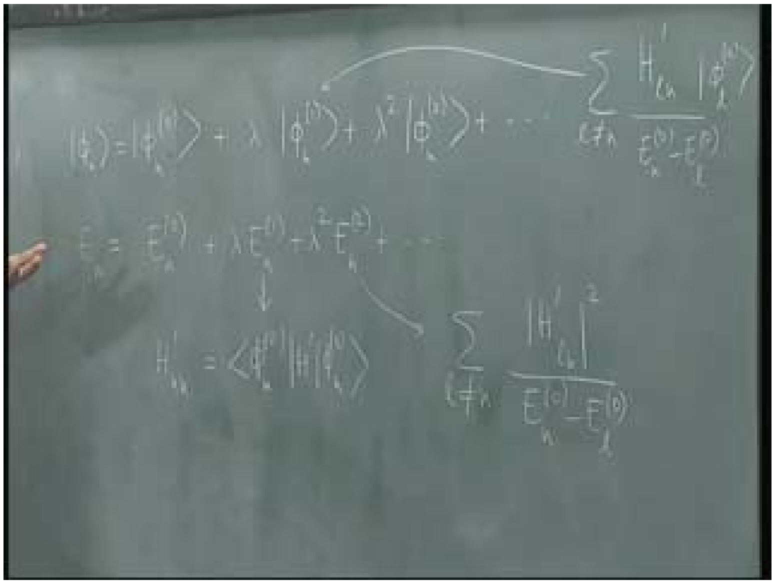

$$|\psi_n\rangle = |\phi_n^{(0)}\rangle + \lambda|\phi_n^{(1)}\rangle + \lambda^2|\phi_n^{(2)}\rangle + \cdots$$

$$\sum_{\ell \neq n} \frac{H'_{\ell n}|\phi_\ell^{(0)}\rangle}{E_n^{(0)} - E_\ell^{(0)}}$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots$$

$$H'_{nn} = \langle\phi_n^{(0)}|H'|\phi_n^{(0)}\rangle$$

$$\sum_{\ell \neq n} \frac{|H'_{\ell n}|^2}{E_n^{(0)} - E_\ell^{(0)}}$$

But you can do a perturbation expansion. If phi $_{n}$ $^{(0)}$ is the eigenstate corresponding to En 0 in the absence of the perturbation for H $_{0}$. This is assumed to be a complete set of states. These are non-degenerate set of eigenvalues. Then, the nth energy level is given by a perturbation series of the form En1 + lambda squared En2 + etc. in exactly the same way, phi n is given by phi n (0) + lambda times phi n1 + etc. the idea was that this infinite series for sufficiently small lambda would actually converge to a finite answer and you can compute to any desired degree of accuracy to what these numbers are. We had found formulas for these. We found that En1 was nothing but the matrix element in the unperturbed basis of the perturbation. This by definition is H prime $_{nn}$. So that was the first order correction to the energy. The second order correction to the energy was a little more complicated. This was a sum over all intermediate sates l not = n, and the matrix element H prime $_{ln}$ squared divided by En $^{(0)}$- El $^{(0)}$. So you had an energy denominator. The difference between unperturbed energy levels and on top, the weight associated with this energy denominator was the square of the modulus of this off diagonal matrix element, H prime. The state vector was = a summation l not = n, H prime ln over En $^{(0)}$ - El $^{(0)}$ phi l $^{(0)}$. We didn’t write down the second order calculation for the wave function for the state vector but it will involve 2 of these intermediate states and so on.

So, there would be a second sum, m not = n, En $^{(0)}$ - Em $^{(0)}$ in the denominator and so on. So the important thing to note is that the energy eigenvalues proceed in a very systematic way. The first term is the just diagonal elements of the perturbation. The second one involves the square of the matrix elements; the off diagonal elements with a single energy denominator. Then next one will involve higher powers of such products of such matrix elements divided by 2 energy denominators and so on. Now we found this result by imposing the requirement that just as phi n (0) is normalized, this phi n too is normalized here. There is nothing arbitrary about it. It’s normalized at every order of perturbation theory. Now of course, there are situations where the first order correction may vanish identically. For instance, if the perturbation doesn’t have diagonal matrix elements at all, then you have you start with the second order correction, etc. now when does this whole thing converge? It’s clear that the conversion is going to depend on this quantity (Refer Slide Time: 11:31).

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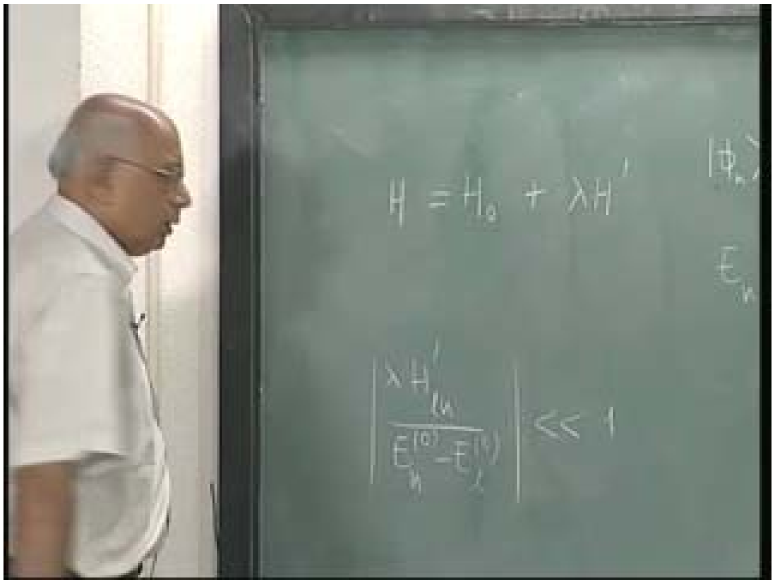

So in general the assumption is that all the off diagonal matrix elements are sufficiently small compared to the differences in energy levels. Then this series has a hope for convergence. This is not a rigorous proof because we don’t know what these general coefficients are. But on the face of it, it seems, looking at the structure of these terms that if this is sufficiently small, you are going to be in good shape. So what you need is, you are going to be in good shape for sufficiently small lambda. The difficulty arises when this is 0. When you have a degenerate state, you don’t know what to do because this is going to become infinite. It’s going to blow up here and then the question is: what are you going to do in such a situation? Before I do that, let me give some examples of perturbation theory. Let’s take a couple of examples and you can see how these formulas are applied.

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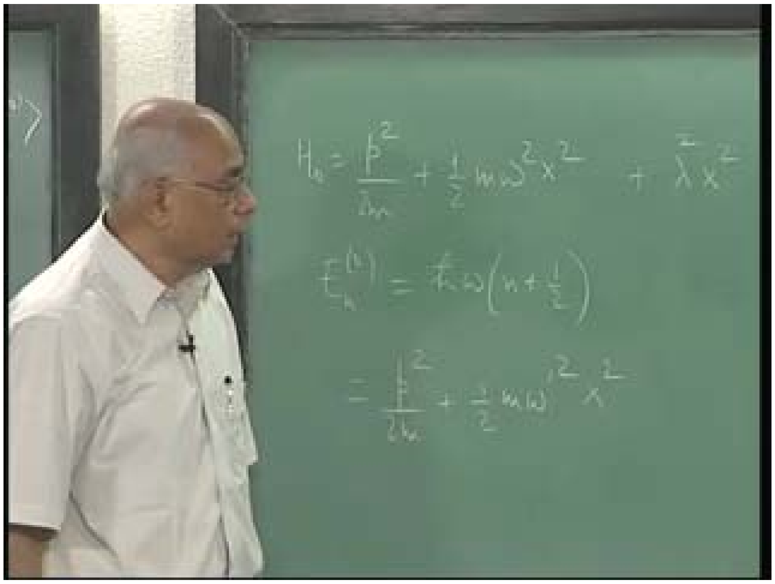

So the simplest example we looked at for instance was the harmonic oscillator where H $_0$ is p squared over 2 m + 1/2 omega squared x squared. In this case, we know that En 0 is h cross omega (n + ½). So those are the exact levels and then you can go on adding terms to this. Suppose you add a lambda x to it, you can compute what's going to happen. Just to see how good perturbation theory is, you can do perturbation theory and then do the problem exactly. How do you do that exactly? You complete squares. It's just a displaced harmonic oscillator. So all it does is to shift the potential and change the 0 level of the potential. So that problem can be actually completed analytically by defining some x prime as (x + shifted value) and completing squares. You could also formally put it into this perturbation expansion and see what happens.

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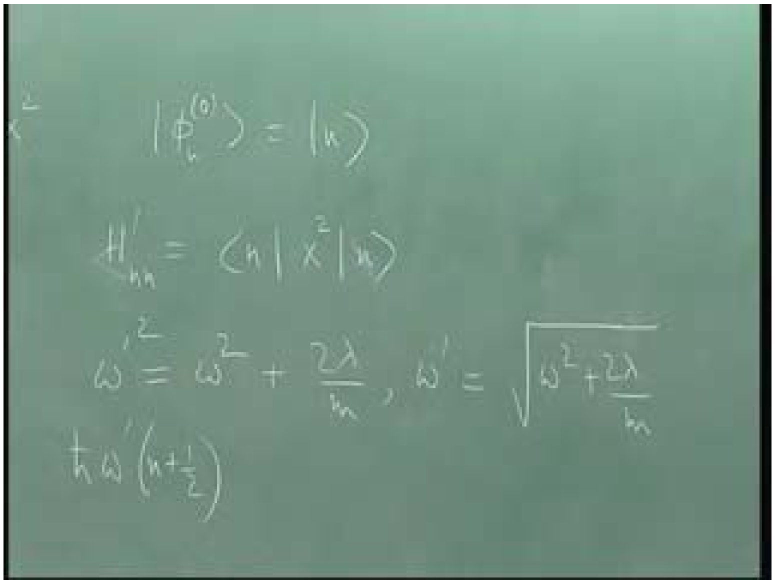

$|\phi_n^{(0)}\rangle = |n\rangle$

$H'_{nn} = \langle n| x^2 |n\rangle$

$\omega'^2 = \omega^2 + \frac{2\lambda}{m}, \; \omega' = \sqrt{\omega^2 + \frac{2\lambda}{m}}$

$\hbar\omega'(n+\frac{1}{2})$

And as far as the oscillator is concerned, the best representation to use is simply phi $_n$ $^{(0)}$ are just the unperturbed oscillator states. H prime nn is <n| x |n>. We write this in terms of raising and lowering operators; a and a dagger. You can see that the first order term is going to be 0 since x does not have diagonal matrix elements. Neither a nor a dagger has diagonal matrix elements. a connects a state n on the left. You must have an n -1 because a lowers and for a dagger, you must have an n +1 on the left. Otherwise these matrix elements are 0. So the diagonal elements are 0 but the second order terms are going to contribute here. I leave it to you as a simple excise to show to what this whole thing is is going to become. Incidentally, we know that when you complete squares you are going to get a lambda squared term.

That's going to be the change in the energy. Now because of that, the perturbation series will actually terminate in the second order term. So I leave you to work this out and show that in this problem which you can solve analytically compare it with what happens if you use the perturbation series. What happens if this perturbation had been x squared? Of course, it is not 0 because it is a + a dagger squared and there are going to be terms like aa dagger and a dagger a which are going to contribute. So here, the first order correction is not 0 and there would be other orders too. Do you expect this to terminate as a power series in lambda? No. why not? Do you think they may not be bound states? Lambda is positive. It's another harmonic oscillator. So what's going to happen? So I can write this as = p squared over 2 m + 1/2 m omega prime squared x squared. The exact energy levels are 1/2 H cross omega prime times n + ½. Do you thing that's going to terminate as power series in lambda? What's omega prime squared in terms of omega? It's omega squared + 2 lambda over m. so the energy levels are going to be H cross omega prime into n + ½ and omega prime is just root of omega squared + 2 lambda over m. So it is not going to terminate because it has got a square root.

Therefore, when you do a binomial expansion in powers of lambda over omega squared which is supposed to be small; this is going to go on forever. What's the physical interpretation here? I just change the spring constant. That can lead to a perturbation series which goes on forever because it's not analytic. When I do a binomial expansion, it will show all possible powers although the exact answer is trivial to write down in this case. So you must watch for things like this. By the way, would it still be true if i had written a lambda squared and not lambda to make sure it's positive? Yes. Except now, only the even powers are going to appear. So nothing changes. It's still going to show all even powers of lambda when i expand. What if I have lambda x cubed as a perturbation?

Well, it's clear the first order term is going to be 0 because this thing is cubic and therefore you don't match powers of a and a dagger in the diagonal. There are no diagonal elements at all. There is a correction to first order but we know this potential is actually not bounded from below. So although the perturbation series will give you a formal answer, we have to take this with a pinch of salt. The exact answer is very different. There are no rigorous bound states in this problem at all. If I have lambda x to the power 4, that's a quadratic oscillator. i can then compute what happens and what's going to happen to various energy levels even though, technically speaking the x 4 has problems. Let's look at a realistic case. Suppose, you have 2 electrons instead of 1 electron, like in the helium problem and then ask what's going to be the energy levels, let's see if this can be solved exactly. This was one of the first problems to which perturbation theory was applied.

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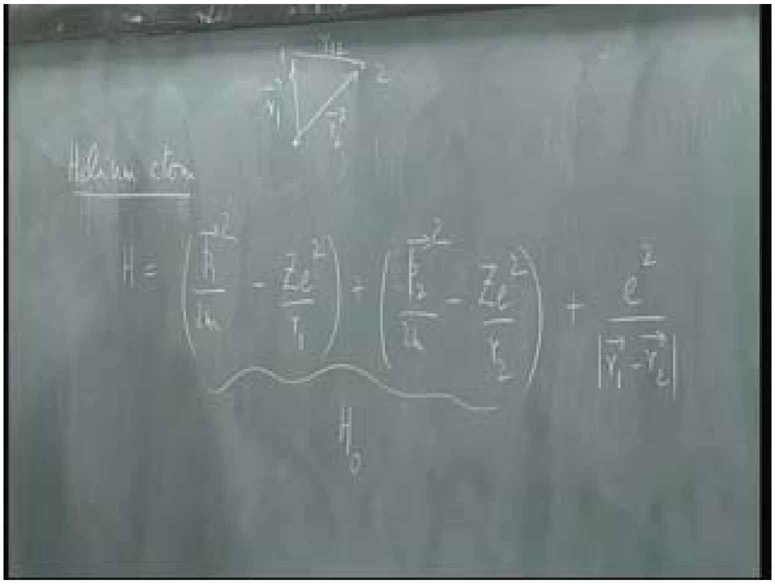

Helium atom

$$H = \underbrace{\left(\frac{\vec{p}_1^{\,2}}{2m} - \frac{Ze^2}{r_1}\right) + \left(\frac{\vec{p}_2^{\,2}}{2m} - \frac{Ze^2}{r_2}\right)}_{H_0} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

So what does the helium problem look like? We look at the ground state wave function just for simplicity. What's it going to look like? You have a nucleus and then you have electron 1 and electron 2 in orbit around it. Let's say the coordinate of electron1 is r1 and the coordinate of electron2 is r2. We write down the Hamiltonian of the system. Its p1 squared over2 m - Ze squared over r1 if Z is the nuclear charge, 2 in the case of helium .so that's for electron1. And then there is a p2 squared over2 m - Ze squared over r 2 for the secondone. There is a Coulomb repulsion between the 2 electrons which you have to put in. and its+ e squared over modulus r1 - r2. That's this (Refer Slide Time: 22:36), r_{12}. This is the Hamiltonian of the system. Now of course, if we didn't have the second electron, the problem is exactly solvable. You get hydrogenic levels. It's the same for the other case too. So these 2 together constitute an H_0 and that's solvable completely. Because the 1st portion of the Hamiltonian commutes with the 2^{nd} portion. It's like 2 independent sets of coordinates. All 1 coordinates commute with the 2 coordinates and you can diagonalize the 1 and the 2 simultaneously. Now what's the ground state energy level? It's going to be -1 over n squared in Rydberg units and now it's going to be twice that. So electron 1 would have got a certain ground state, 2 would have got a certain ground state and this is just twice that ground state. So let's call that energy E_0. We know what this energy level is. By solving the 1 electron problem, you can solve this as well. They are completely uncoupled here.

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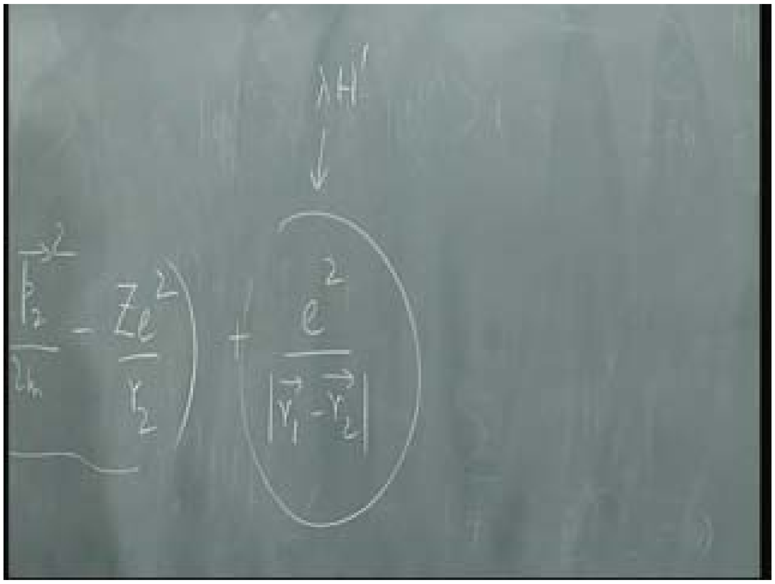

e squared over |r1 – r2| is the equivalent of lambda H prime. e squared would play the role of the perturbation parameter lambda. So what would be the first order correction? That's the question we have to answer.

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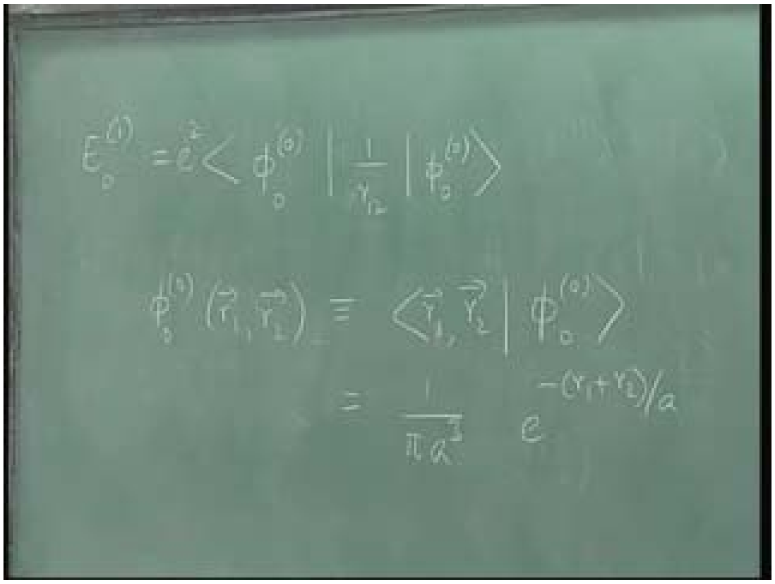

$$E_0^{(1)} = e^2 \left\langle \phi_0^{(0)} \right| \frac{1}{r_{12}} \left| \phi_0^{(0)} \right\rangle$$

$$\phi_0^{(0)}(\vec{r}_1, \vec{r}_2) \equiv \left\langle \vec{r}_1, \vec{r}_2 \middle| \phi_0^{(0)} \right\rangle = \frac{1}{\pi a^3} e^{-(r_1+r_2)/a}$$

So the correction E1 = e squared phi $_0$ (unperturbed) 1 over r12 phi $_0$ $^{(0)}$. That's the correction. Phi 0 refers to the ground state of the system and the superscript ^{0} means completely unperturbed. Now all we need to know to do that, is the wave function of the electron in the ground state. Now what's the wave function of the hydrogen atom in the ground sate of the electron? Well, we need some representation in which to calculate this quantity? And what basis would you choose? The position basis or the moment basis? Position. So we know the wave function in position space. The wave function phi $_0$ 0 (r1, r2) = r1 r2 phi $_0$ 0. By definition it's the abstract ket vector overlapped with these position eigen states. r1 refers to first electron r2 to the second electron. By the way, I have ignored spin of the electron here. That too must be taken into account. For the moment, we have ignored it. Now what's the ground state of the electron in the hydrogen atom?

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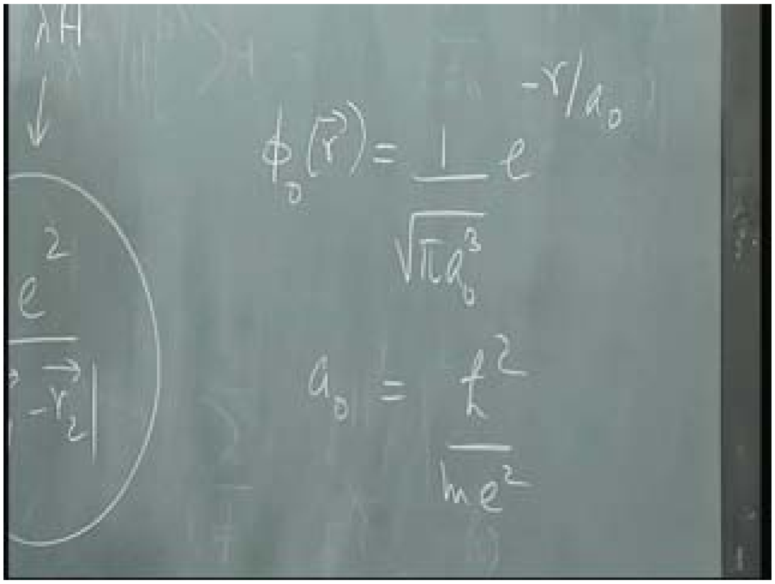

If you got a single electron, then the ground state wave function phi $_0$ (r) = some normalization e to the - r over a $_0$ where a $_0$ is the Bohr radius and the normalization is square root of pi a $_0$ cubed. This is the ground state wave function in the state in which the principle quantum number n is 1, L is 0 and m is 0. It's just an exponential decay. a $_0$ is the Bohr radius. What's the Bohr radius in these units? It's h cross squared over m e squared. That's the Bohr radius in the units in which I am working.

If I put in a nuclear charge z, what happens to this? Does the Bohr radius increase or decrease? It decreases. It gets closer. So it decreases by1 over z factor. So it becomes a = a $_0$ over z. the more the charge in the nucleus, the tighter the whole thing is going to be. So now what's the wave function? This is unperturbed. It's as if the2 electrons were separate. So each electron has a wave function 1 over square root pi a cubed e to the - r over a. so what is this going to be? It's going to be 1 over pi a cubed e to the power - r1 + r2 over a because it's just the product of the 2 wave functions. This is a direct product. State it's just position space eigen ket r1 for the first term and direct product with r2 for the second term. So the each wave function is e to the - r1 over a e to the - r2 over a and the combined wave function is a product of these 2 in the unperturbed basis. So it's just e to the - r1 + r2 over a.

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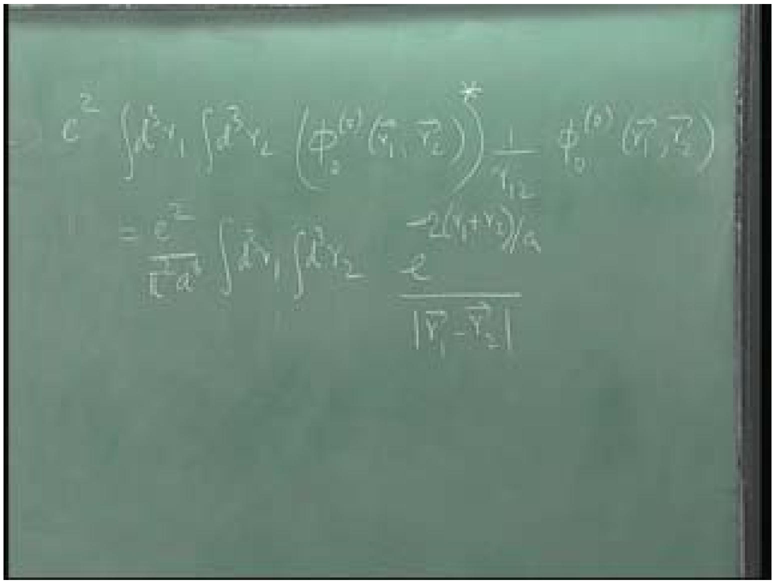

$$e^2 \int d^3r_1 \int d^3r_2 \left(\phi_0^{(0)}(\vec{r}_1, \vec{r}_2)\right)^* \frac{1}{r_{12}} \phi_0^{(0)}(\vec{r}_1, \vec{r}_2)$$

$$= \frac{e^2}{\pi^2 a^6} \int d^3r_1 \int d^3r_2 \frac{e^{-2(r_1+r_2)/a}}{|\vec{r}_1 - \vec{r}_2|}$$

E_0 $^{(0)}$ = e squared over and what's this integral? What does this stand for now? Remember, if you are going to if you are going to write this matrix element in the position basis, then there is an integration. The final answer is not going to depend on r1 or r2 or anything it's integrated over completely. If you understand that, then you understand this notation completely. so let's write this as integral d3 r1 for the first term, an integral d3 r2 for the second term, and then wave function phi $_0$ $^{(0)}$ (r1, r2) star complex conjugate because you want the bra and then the perturbation 1 over r12 and phi $_0$ $^{(0)}$ (r1, r2). So it stands for this integral. It's a number. It cannot depend on r1 or r2. So this whole thing becomes e squared over pi squared a to the power 6 and integral d3 r1 integral d3 r2 e to the power -2(r1 + r2) over a divided by |r1 - r2|. This is not such a simple integral to do because r1 and r2 are kind of mixed up with each other.

That's the first order correction to the energy. If you can compute this integral, then you know what the energy is going to be to first order and E squared. How does one do an integral of this kind? What coordinate system can we choose? Normally if you had just a single e to power - r or something you would use spherical polar coordinates the matter is over but now you got that the modulus r1 - r2 in the denominator. Does that formula remind you of something? It looks like the electrostatic energy of something or the other. What sort of charge density? Suppose you have a charge distribution and you want to calculate its electrostatic self-energy, then you take1 volume element here another volume element there and ask product of the2 charges in these volume elements divided by the distance. That's going to give the electrostatic potential energy. So, it looks very much like the electrostatic potential energy of a charge distribution which is given by 1 over pi a cubed e to the power - r over a. a kind of exponential damped charge distribution.

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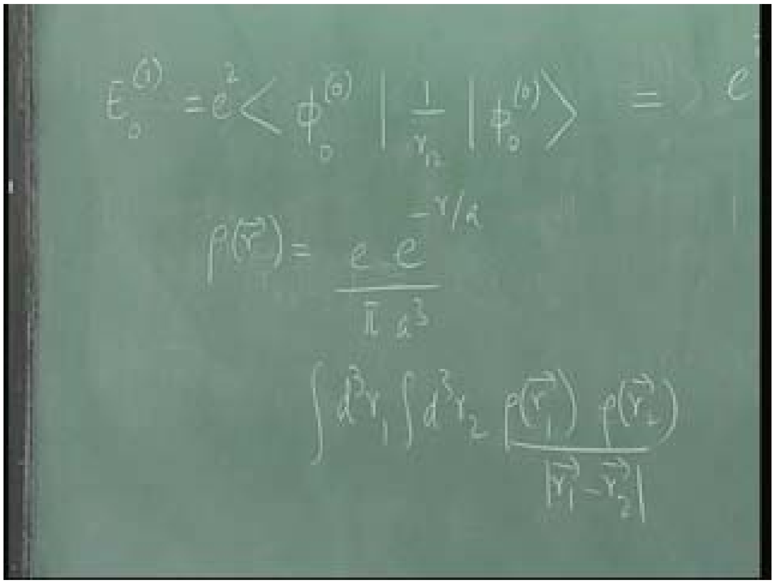

$$E_0^{(1)} = e^2 \left\langle \phi_0^{(0)} \right| \frac{1}{r_{12}} \left| \phi_0^{(0)} \right\rangle = e$$

$$\rho(\vec{r}) = \frac{e\, e^{-r/a}}{\pi a^3}$$

$$\int d^3r_1 \int d^3r_2 \frac{\rho(\vec{r}_1)\, \rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}$$

So if I have a charge distribution rho (r) in space which = e to the power - r over a e (electronic charge) over pi a cubed. It's exactly that. Because, the electrostatic self-energy is going to be d3 r r1 d3 r2 rho of r1 d3 r1. That gives is the charge in volume element dv1. This is the electrostatic energy apart from a 1 over4 by epsilon $_0$. So it really looks like these are the exponential damped charge cloud and then this overlap integral is giving you the potential energy. We haven't taken into account some very crucial things here. We haven't taken into the spin of the electrons. What other factor have we not taken it account here, related to the fact that the electrons are spin ½? We took the wave function to be just a product of the wave function of electron 1 times product the wave function of electron 2.

But of course the electrons are indistinguishable. So this wave function cannot be the right one. It must be antisymmetric under the exchange of the2 electrons. You must include the spin also. So that important factors haven't been taken into account. This is not quite the wave function. You need what's call the Slater determinant. It must be antisymmetric. It depends on spin state the entire wave function. Now let me remind you that if you have 2 spin-1/2 particles, they can either be in a total S = 0 state or total S =1 state. If they are total S = 0 state, then the spin wave function is antisymmetric and the spatial wave function is symmetric. The ground state would be the correct state and that's what we have taken into account. The fact that this position space wave function is symmetric is just e to the - r1 by a e to the - r2 by a is good enough for the ground state calculation. So what we are doing is calculating correction to the ground state in which indeed the2 electrons are in spin S = 0 state. If you looked at excited states, then it's a different story. You have to take these possibilities into account. So for the ground state this is a good approximation. We still have to compute the integral. How would1 do that? We need a formula for this and that's familiar to us from electrostatics. So let me go back and remind you of what you know from electrostatics.

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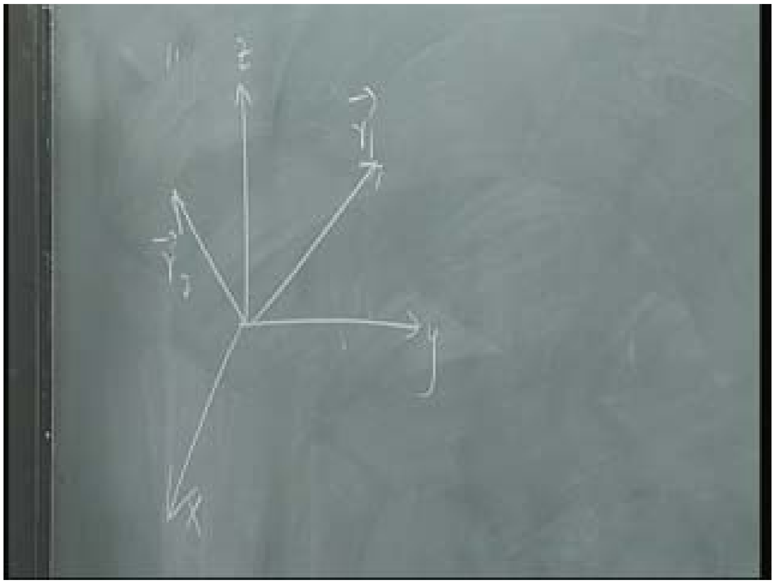

We know that if you have 2 vectors r1 and r2 in electrostatics, let's look at a coordinate system xyz in this fashion. The dihedral angle between r1 and r2 is some gamma, say. Then modulus r1 - r2 whole squared mod squared is r1 squared + r2 squared -2 r1 r2 cosine of the angle gamma. But there is a formula for the cos gamma and what's that?

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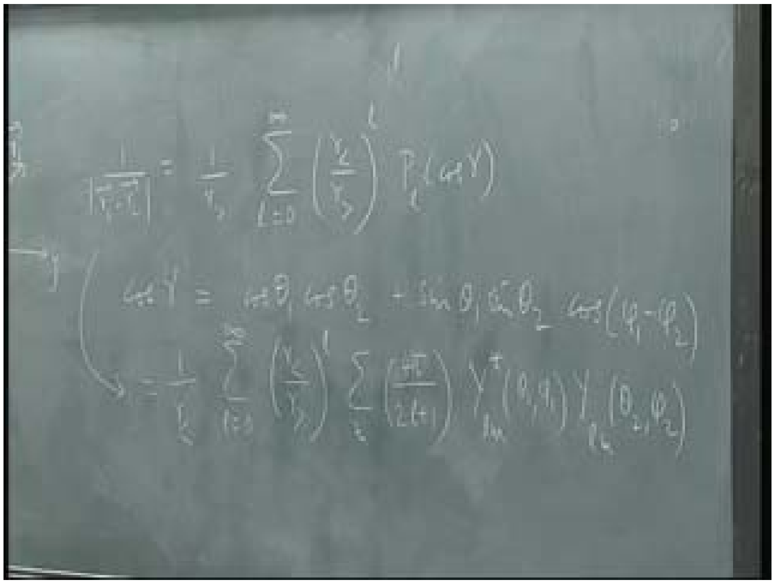

Well, we know the following. 1 over r1 - r2 = a summation. It’s expanded in a power series in powers of r2 over r1 if r2 is smaller than r1. But if r1 is smaller than r2 in magnitude, then you expand in a power series of r1 over r2. in both cases, this can be written as1 over r, the larger of2, a summation l = 0 to infinity r small over r larger to the power l over all the integers multiplied by coefficients which are going to depend on the cosine of the angle between the 2 multiplied by Pl (cos gamma). These are the Legendre polynomials. In fact, this is one way to introduce the Legendre polynomials. they are the coefficients in the expansion of 1 over square root of r1 squared + r2 squared -2 r1 r2 cos gamma. the answer is a series of polynomials in cos gamma and the coefficients are r - over r + grad r less over r greater to the power l. so all we need to know is what’s the cosine of this angle in terms of the polar angles of r1 the polar angles of r2? That comes from a following formula in spherical trigonometry. There is a very well-known formula in spherical trigonometry. So cos gamma is cos theta1 cos theta2 + sin theta1 sin theta2. these are the polar angles of vectors r1 and r2.

Of course there must be a dependence on the Azimuthal angles as well and cos phi1 - phi2. That’s a well-known addition theorem. if you got 2 arbitrary vectors and the angle between them is the dihedral angle between them is gamma, then the cosine of this gamma is given in terms of the cosines of the polar angles and Azimuthal angles of the 2 individual vectors. This is just a special case of the addition theorem for Legendre polynomials because cos gamma is P1 (cos gamma). P1 (x) is x. but there is a general theorem for Pl cos gamma itself. So 1 over |r1-r2| can be written as1 over r less, summation l = infinity r less over r greater to the power l, summation over m and 2 l +1. There is also a 4 pi over 2 l +1 which comes from the normalization factor. Then its Ylm theta1 phi1 star Ylm theta2 theta2 where Ylm’s are the spherical harmonics. this is called the addition theorem for spherical harmonics. So you can write Pl cos gamma, the general l in terms of these Ylm’s. If you put l =1, then you end up with the original addition theorem for these dihedral angle.

These quantities are square root of 2 l +1 over 4 pi times P_{lm} (cos theta1) e to the power -im phi1 and so on for the other term. So whatever it is, one can put this into that expression and then do the integrals. So go to spherical polar coordinates for each of them. It’s in a nice factored form here. Therefore you put that in here and the price you pay is that there is a summation over l. So the price you pay for factoring this into something which dependence on coordinates of r1 and r2 is that it becomes a summation. Since there is an exponential makes it easy to calculate these quantities. Finally, there were just some powers of l multiplied by exponentials. You have to be careful about convergence. You must be careful when you integrate over r1 and r2. You must make sure that when you use that expansion, you need one expansion in the cases where r2 is less than r1 and the other when r2 is bigger than r1.

It’s a numerical thing to compute it. It doesn’t include all these other corrections. It doesn’t include the effect of spin, the Pauli exclusion principle and so on. And yet it gives a very good answer. Of course, one can refine it. We know how to compute the helium problem. We know how to compute the energy levels to an arbitrary degree of accuracy using this. But as you can see, at some stage it gets numerical beyond a certain point. You need to know how to do these integrals. You get to higher orders and it will get worse. So this is not the most efficient way of finding the energy levels of the helium atom. You use what's called a "variational method". So you pretend that z is a variable quantity and then you minimize the ground state energy with respect to these variational parameters.

And now people have done this using many variational parameters simultaneously. For many electron systems, the best way of finding these energies is by variational methods. The answers are known to very high accuracy. So this is just an indication of how perturbation theory would operate in such problems. Let's go on to what happens if you have a degeneracy in the problem. So we need to address this. Instead of writing the formulism down, let me just indicate the way of doing this.

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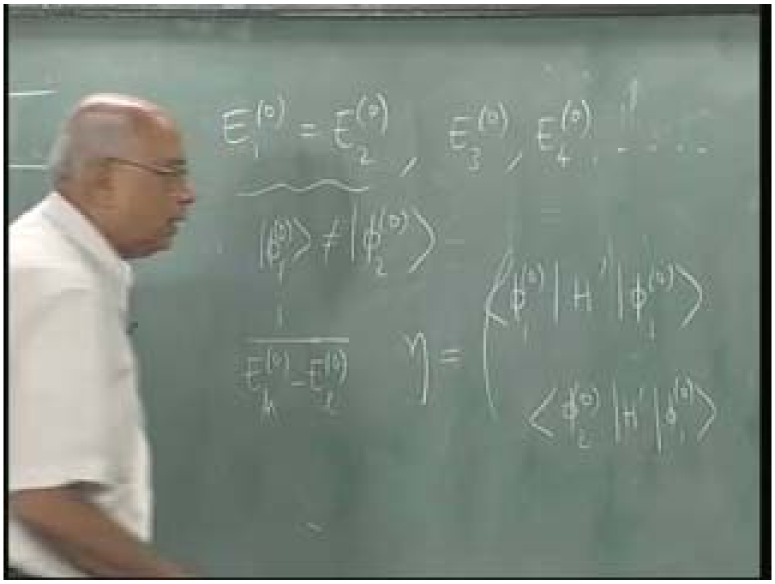

Suppose you have a situation where one of the energy levels is degenerate. So the unperturbed levels are E1 0 = E2 0 and then E3 0, E4 0 and so on. This is what the unperturbed levels look like. There is a ground state that's degenerate or one state that's degenerate and then it goes on. For convenience, I have taken these 2 to be degenerate but anywhere in between, you could have a degeneracy and it doesn't have to be a 2 fold degeneracy. it could be 3 fold, 4 fold, etc of any finite order of degeneracy. Now in a problem like this, corresponding to this there exist an eigen state phi1 0 and an eigenstate phi2 0 which are not = each other. This is what is meant by degeneracy. There exist2 linearly independent eigen states corresponding to the same value of the eigen value. and then of course when you do the energy denominator, I want to find the correction to E1 0, i run into trouble because i have a summation over l not equal to n. when I sum over the value too, this is going to blow up. So the question is: how do I get rid of this problem?

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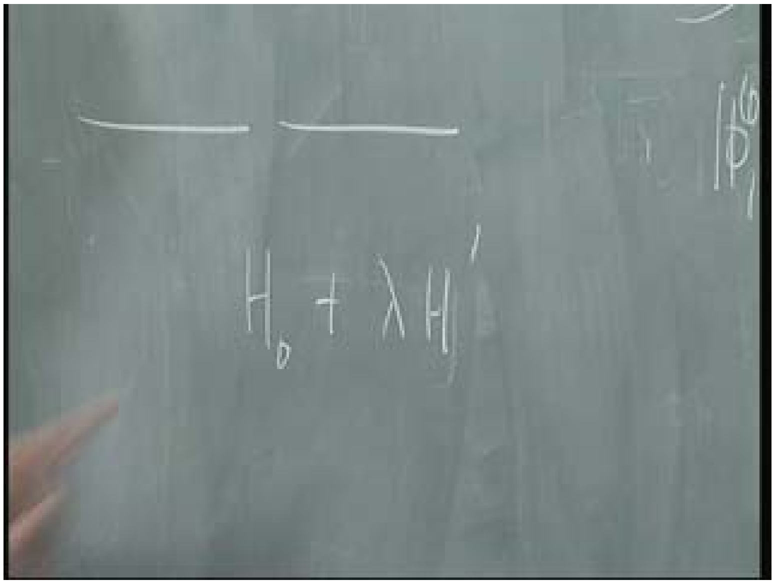

So what one does is to say that the Hamiltonian is H $_0$ + lambda H prime and the difficulty arises because of this energy denominator En (0) - El (0) when n is1 and l is2 or vice versa. These 2 are exactly the same. So what you have to do is to note that, in this subspace spanned by these 2 vectors, diagonolize the problem exactly. So what will the perturbation look like?

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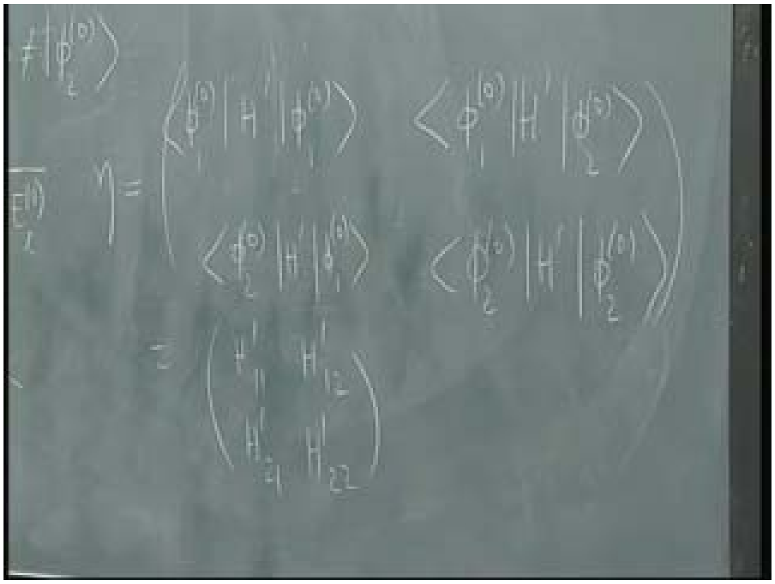

The perturbation H prime is going to have <phi1 0| H prime |phi1 0>. In this subspace it's going to look like phi1 0 H prime phi2 0 and then the conjugate of that. This is what the Hamiltonian matrix is going to look like in this subspace. So let me call this eta. The idea is to diagonlizes eta. So let me write this as H prime11 H prime12 H prime21 H prime22. The idea is to diagonolize this and then use the eigen vectors corresponding to the diagonolized form this. You can certainly diagonolize a2 by2 matrix without difficulty. So use that as part of the unperturbed basis. So as far as the subspace spanned by these2 degenerate eigenvalues is concerned, the eigen degeneracy is lifted. You found the exact eigen values and the exact functions corresponding to these 2 states and use those as part of your unperturbed basis. So that's the basic trick.

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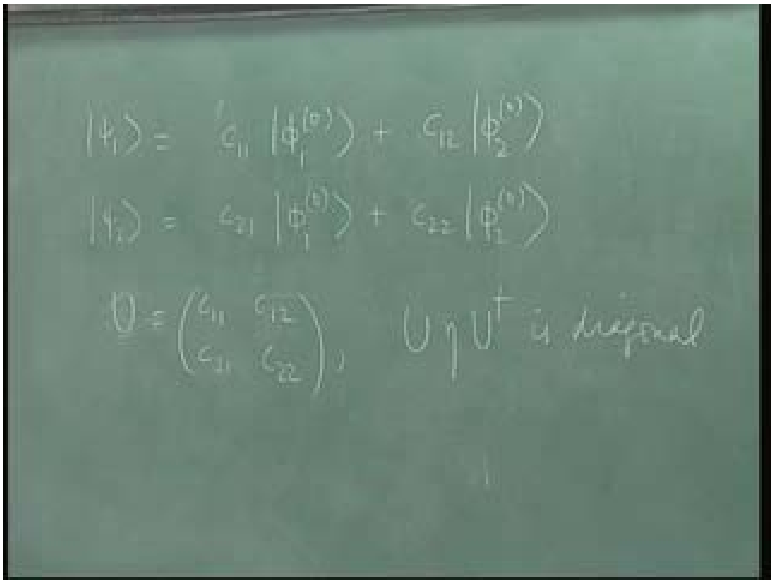

$$|\psi_1\rangle = c_{11}|\phi_1^{(0)}\rangle + c_{12}|\phi_2^{(0)}\rangle$$

$$|\psi_2\rangle = c_{21}|\phi_1^{(0)}\rangle + c_{22}|\phi_2^{(0)}\rangle$$

$$U = \begin{pmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{pmatrix}, \quad U\eta U^{\dagger} \text{ is diagonal}$$

So what would one do? Well, lets say psi1 = some coefficient C11 phi1 0 + C12 phi2 0 and psi2 = C21 phi1 0 + C22 phi2 0. Instead of using phi1 0, phi2 0, phi3 0, phi4 0 etc as my unperturbed basis, i use psi1, psi2, phi3 0, phi4 0 etc as my basis. But I must choose t the Cij's in such a way that the Cij matrix diagonolizes this eta. So that the basic trick. This is a Hermitian matrix (Refer Slide Time: 51:10). So this is the complex conjugate of that and it's a Hermitian matrix. These are real numbers. Therefore you can always diagonolize it by a unitary transformation. Just as a real symmetric matrix can be diagonolized by an orthogonal transformation, a Hermitian matrix can be diagonolized by a unitary transformation. So I insist that this matrix C11 C12 C21 C22 be a unitary matrix. Let's call the matrix U = C11 C12 C21 C22 such that U eta U dagger is diagonal. So I choose my C11 C12 etc in such a way that this is a unitary matrix and it diagonalizes this eta. The job is done. What I should use instead of E1 0 and E2 0, I must choose the actual diagonalised eigen values. What are the eigen values of this matrix?

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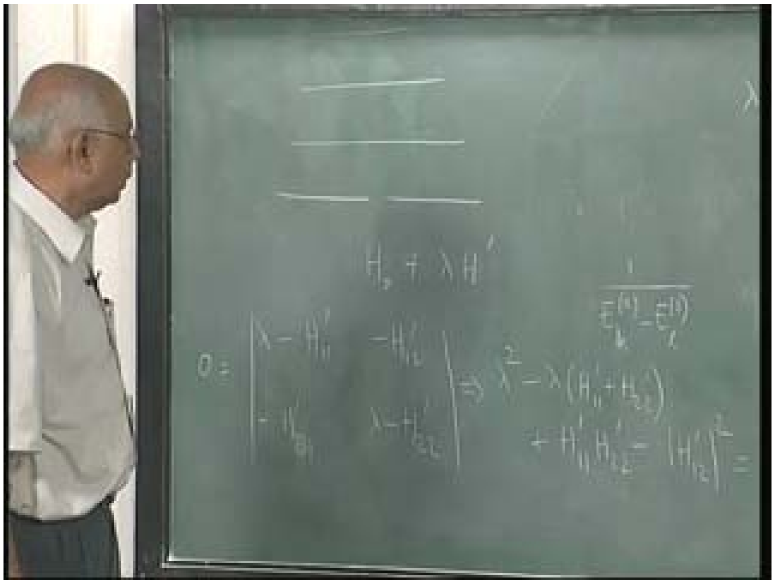

$$H_0 + \lambda H'$$

$$\frac{1}{E_k^{(0)} - E_l^{(0)}}$$

$$0 = \begin{vmatrix} \lambda - H'_{11} & -H'_{12} \\ -H'_{21} & \lambda - H'_{22} \end{vmatrix} \Rightarrow \lambda^2 - \lambda(H'_{11} + H'_{22}) + H'_{11}H'_{22} - |H'_{12}|^2 =$$

It’s lambda - H11 prime - H12 prime, H12 prime H21 prime, lambda - H22 prime. this 0 implies lambda squared - lambda H11 prime + H22 prime + H11 prime H22 prime - mod H12 prime squared = 0.

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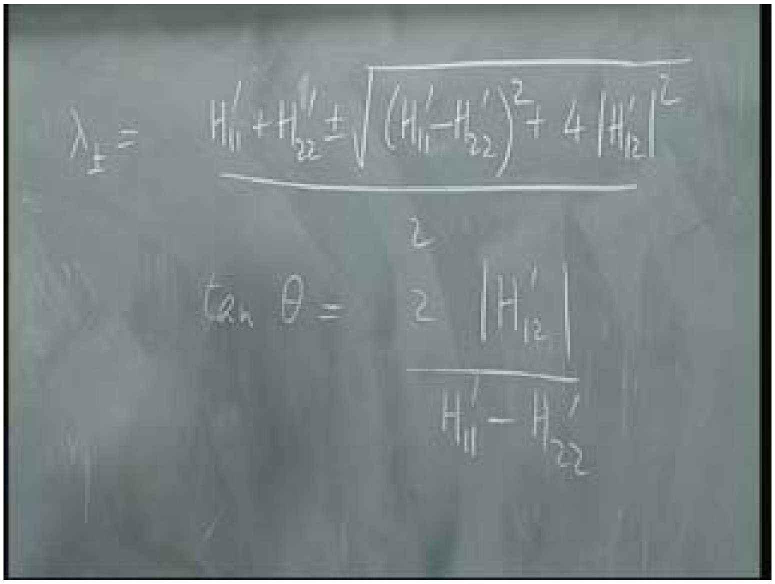

$$\lambda_\pm = \frac{H'_{11} + H'_{22} \pm \sqrt{(H'_{11} - H'_{22})^2 + 4|H'_{12}|^2}}{2}$$

$$\tan\theta = \frac{2|H'_{12}|}{H'_{11} - H'_{22}}$$

If diagonolize it, the eigen values lambda + or - = H11 prime + H22 prime + or - square root of (H11 prime - H22 prime) squared + 4|H12 prime| over2. We can find the eigenvectors corresponding to this. That's a very well-known formula for the 2 by 2 case. So I define tan theta = twice modulus H12 prime over H11 prime - H22 prime. So psi 1 is just cos theta over 2 + sin theta over2 and psi 2 is - sin theta over2 and cos theta over 2. So for a 2 by2 problem, this appears so often that one remembers this very standard thing here. So now you are guaranteed that you know the exact eigenvalues and use that as part of your basis. And then the job is done where no degeneracy is left anymore. So what has actually happened is that the perturbation has lifted the degeneracy and has created 2 new energy levels from it which are not degenerate with each other. I use the eigenfunctions corresponding to that exact Eigen function. There is no perturbation here. This square root is taken to all orders. You actually know what this is. Now you can generalize this if you have 3,4,5 etc to any number of any finite degeneracy. So this is how degenerate case would be handled in many famous examples where you have such kinds of finite degeneracy and then it's lifted by doing this first here. But all this is still time independent perturbation theory.

We have still not addressed the question of what happens if you put in time dependence in the Hamiltonian if you pump from outside, you supply energy or remove energy. The last thing i want to do is to address that because that's what is going to tell us what causes transitions between unperturbed energy levels whereas here, what we are trying to do is there is a fixed perturbation. We know what the unperturbed levels are. We are trying to compute what happens and the effect of the perturbation. So both degenerate and non-degenerate cases, we looked at very briefly but the real interest now in time dependent problems would be to look at transition rates. Again we are going to do things to first order in perturbation theory. We are going to arrive at a rule called the "Fermi golden rule" which is essentially going to tell us what the transition rate is to go from one level to another under a given perturbation. So let's do that last.

(Conversation between student and professor): you see, if you had a non-degenerate problem and these were your energy levels, then under perturbation, this level may go here, this level goes here, this one goes there and so on (Refer Slide Time: 58:21). We can compute it to any order. now the problem was you had a degenerate level here, 2 of them sitting right on top of each other, then the strategy is to say when i include the perturbation H prime, then because H prime became the total Hamiltonian which has off diagonal elements as well, this splits automatically into this. These are the 2 energy levels (Refer Slide Time: 58:43).

Now I calculate what's the effect of the perturbation that we have added to this entire system. But please notice that these are not the exact energy levels under the perturbation because physically, what's happening when you do second order perturbation theory, all the unperturbed energy levels are affecting each given energy level. Because remember the energy denominator. Because there is a summation over all the unperturbed levels affecting each of these levels. So what we did was to pretend, in this degenerate perturbation theory that none of these fellows exist. Then I put in the H prime and diagonalized only this portion (Refer Slide Time: 59:35). I used this as part of my basis now. Instead this (Refer Slide Time: 59:40), I use these levels as my basis and then ask: what's the effect of perturbation? So, all of them are going to be shifted once again. But these are no long at degenerate. Therefore the energy denominators don't play a role. So that was the strategy. A second order perturbation theory really is a statement of the fact that when you apply a perturbation, the entire unperturbed spectrum affects each level in the perturbed spectrum. Even the distant ones. Even they have a role to play because it depends on the matrix elements.

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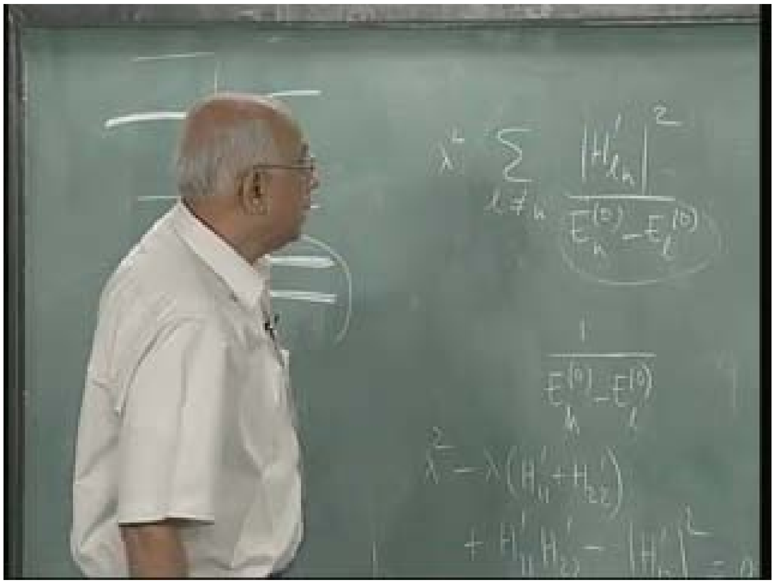

Please remember that the second order correction to the energy level n went like lambda squared summation l $_0$ = n, H prime $_{ln}$ squared over En $^{(0)}$ - El $^{(0)}$. So the n th energy level got affected by all the other l's here to an extent, which depends on the difference between the energies. Of course, if this difference is very large, the distant levels from these n are not going to play much of a role but how much or what role they play depends on how big this matrix element is. So it depends on what connects to what. If H prime has a strong matrix element between 2 particular levels, that's going to significantly contribute to the correction due to the perturbation. So finally physically, you can see what is happening.

Does this operator (H prime ln) connect 2 different levels or not? Is there a non-vanishing matrix element and if so how big is it? These mod square of this matrix element in atomic physics are often called oscillator strengths because this whole thing plays a very fundamental role in atomic physics when you do perturbation theory for energy levels. This is like some given weight factor but these strengths control what connects to what. So that was a strategy used here and i did this for the doubly degenerate case. But for any finite degeneracy, you can use the similar kind of thing. Now of course, it’s possible that the first order correction, this degeneracy is not lifted in the first order. It could go on to the next order and so on and so forth. That too can happen but it gets a little more algebraically complicated. But the principle is clear. The principle is that in that subspace, you diagonalize and find the exact levels to that order pretending nothing else exist and then use that as the basis. That was the strategy. So let me stop here. Thank you!